

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 131

APPLICATION OF THE INTERFEROMETER TO GAS ANALYSIS

BY

JUNIUS DAVID EDWARDS, Associate Chemist

Bureau of Standards

ISSUED OCTOBER 6, 1919



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By Junius David Edwards

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I. INTRODUCTION

It is only within recent years that extended practical application of physical methods to chemical analysis has been made. This has been especially true in the case of gas analysis. Progress in developing new and improved methods for gas analysis was slow as long as differentiation by chemical characteristics alone was employed. However, there are quite a number of physical characteristics of gases, such as refractivity, thermal conductivity, heat of combustion, density, viscosity, etc., which offer almost unlimited possibilities for the development of gas-analysis apparatus for various purposes.

One of the most useful of the physical methods which have been developed is that of gas interferometry. Rayleigh¹ first described the essential features of this method. Later, Haber and Löwe² developed what is known as the Rayleigh-Zeiss gas interferometer, which marks the first practical application of the method. Interferometers of the Rayleigh type are now manufactured by Hilger, of London. Although widely used abroad,

¹Rayleigh, Proc. Roy. Soc., 59, p. 201: 1896.

²Haber and Löwe, Zs. f. angew. Chem., 23, p. 1393: 1910.

the number in use in this country has been rather limited—less than their utility would warrant.

The author ³ has described a new method of calibrating the gas interferometer, which greatly simplifies and extends its use. The present paper will discuss the simple relations which exist between the properties of the gases and the indications of the instrument and give examples illustrative of its use.

II. PRINCIPLE OF METHOD

The gas interferometer is essentially a differential refractometer; it measures the difference in refractivity of two samples of gas. The gases are contained in two long (100 cm in one instrument), narrow gas chambers, the ends of which are closed by plane parallel glass plates. White light from an illuminated slit passes through both chambers, after which the two beams combine to produce interference fringes which are observed through an eyepiece. If the composition of the gas in the two tubes is different, the optical paths through the tubes are different, and the interference fringes are displaced from their normal position. The optical path of one of the beams can be adjusted to equality with the other by tilting a glass compensator plate, which is placed in the path of the beam. The angle through which the compensator plate must be turned to bring the two optical paths to equality, as shown by the position of the interference fringes, is a measure of the difference between the refractive indices of the two gases. This adjustment is made by means of a micrometer screw acting on a lever arm attached to the compensator plate. A second set of fringes, produced by two beams of light which pass over the gas tubes and which are fixed in position because the two beams always have equal optical paths, are used as a reference point in much the same way as the cross hair in a telescope. The reader is referred to the more complete descriptions in the literature for further details of the apparatus.

III. THEORETICAL RELATIONS

The refractivity R of a gas is equal to the refractive index minus 1.

$$R = n - 1 \quad (1)$$

It has been shown that the refractivity of a gas is proportional to its density or

$$\frac{R}{d} = \text{constant} \quad (2)$$

³ Edwards, J., *Am. Chem. Soc.*, **39**, p. 2382: 1917.

This relation holds with considerable exactness for gases at ordinary temperatures and within a pressure range of a few atmospheres. From equation (2) the refractivity of a gas can be calculated for different temperatures and pressures by the application of the gas laws, since the density of a gas is proportional to its pressure. When the deviations of the gas from the simple gas laws are important, they can be taken into account, as will be shown later.

The refractivity of a gas mixture can be calculated from the refractivity of the components and the composition of the mixture. In a binary mixture composed of gases having refractivities R_1 and R_2 the refractivity R for any proportion of the two gases is given by equation (3), in which a and $(100-a)$ are the proportions in which they are present.

$$R = \frac{R_1 a + R_2 (100-a)}{100} \quad (3)$$

The available evidence shows that this equation holds with considerable accuracy. For example, the refractivity of air, calculated in this manner from the values given in Table 1 for the refractivities of its constituents is 2915×10^{-7} as compared with the observed value 2917×10^{-7} .

The reading of the interferometer is a measure of the difference in refractivity of the gases in the two chambers. This difference in refractivity can be easily calculated from the preceding relations. If R_1 is the refractivity of one gas at 0°C and 760 mm and R_2 is the refractivity of the second gas or standard of comparison under the same conditions, then the difference of refractivity of the two gases at any pressure p and absolute temperature T is as follows:

$$(R_1 - R_2)_{T,p} = \frac{273}{T} \cdot \frac{p}{760} \cdot (R_1 - R_2) \quad (4)$$

The interferometer reading is determinate only for binary mixtures or their equivalent; mixtures of constant composition, such as air for example, may be regarded as a single component. It is the usual practice where convenient to use one of the components of the gas mixture as the standard gas. In this case the difference in the refractivity of the mixture and one of its components is measured. If R_1 and R_2 are the refractivities of the two gases,

then the change in the refractivity of the mixture (ΔR) for a change of a per cent of one of its components is as follows:

$$\Delta R = \frac{273}{T} \cdot \frac{p}{760} \cdot \frac{a}{100} (R_1 - R_2) \quad (5)$$

Equation (5) also represents the change in the difference between the refractivity of the mixture and any standard gas for the change in composition stated. The symbol ΔR will be used to represent the change in refractivity of the mixture for a given change in composition and the symbol Δr will be used to represent the difference in refractivity between the gases in the two chambers. Under certain conditions ΔR and Δr are numerically equal, but a distinction is made to simplify the discussion of certain problems.

IV. CALIBRATION OF INTERFEROMETER

Each scale division of the interferometer corresponds to a definite value of Δr which is a characteristic of the instrument. If the interferometer could now be calibrated in terms of Δr so that the refractivity difference for any scale reading was known, then its calibration for any gas could be calculated if the refractive index of that gas is known.

The author has described a method of calibration of the interferometer, based on this principle,⁴ which is extremely simple and easy to carry out. To determine the scale reading corresponding to a given difference in refractivity, both chambers of the interferometer are filled with dry air, free from carbon dioxide, and at a definite temperature and pressure. The pressure, and hence the refractivity of the gas, in one chamber is then varied progressively and the scale reading corresponding to each pressure noted. The pressures in the two chambers are p_1 and p_2 and the temperature T remains constant. The refractive index (n_D) of air, free from carbon dioxide, at 0° and 760 mm pressure, as determined by Meggers and Peters,⁵ is 1.0002917.

It follows from equations (1) and (2) that ΔR or the difference in refractivity corresponding to each scale reading (observed reading minus "zero" reading) can be calculated as follows:

$$\Delta R = \frac{273 \times 0.0002917 (p_1 - p_2)}{760 T} \quad (6)$$

⁴ Bulletin Bureau of Standards, 14, p. 473, 1917; J. Am. Chem. Soc., 39, p. 2382, 1917.

⁵ Bulletin Bureau of Standards, 14, p. 697, 1918.

From the curve of refractivity differences determined in the above manner the scale reading corresponding to the refractivity difference calculated from equation (5) can be ascertained and a curve constructed giving the scale reading for any percentage of the gas for which the calibration is desired.

TABLE 1.—Refractivity of Certain Gases

Gas	Formula	Refractivity $\times 10^{-7}$ 0°C—760 mm	"Ideal" refractivity ^a $\times 10^{-7}$ 0°C—760 mm
Air.....		^b 2917	2916
Oxygen.....	O ₂	2706	2704
Nitrogen.....	N ₂	2972	2971
Hydrogen.....	H ₂	1387	1388
Helium.....	He	0342	0342
Neon.....	Ne	0671	0671
Argon.....	A	2809	2807
Krypton.....	Kr	4270	4259
Xenon.....	Xe	7020	6968
Carbon monoxide.....	CO	3347	3346
Carbon dioxide.....	CO ₂	4498	4467
Methane.....	CH ₄	4415	4408
Ethane.....	C ₂ H ₆	7660	7578
Ethylene.....	C ₂ H ₄	7266	7209
Acetylene.....	C ₂ H ₂	6020	5971
Cyanogen.....	C ₂ N ₂	8490	8320
Sulphur dioxide.....	SO ₂	6760	6628
Ammonia.....	NH ₃	^c 3820	3778
Nitrous oxide.....	N ₂ O	5160	5122
Nitric oxide.....	NO	2950	2947

^a See page 9 and 10.

^b Meggers and Peters loc. cit.

^c Preliminary measurement by Cragoe and Peters, Bureau of Standards.

V. REFRACTIVITIES OF THE GASES

It is apparent that the accuracy of this method of calibration is limited among other things by the accuracy with which the refractive indices have been determined. The refractive index of air is known from the work of Meggers and Peters to within a part in a thousand. The refractive indices of most of the other common gases are known with sufficient accuracy to be used for calibrating the interferometer. The tables of refractive indices, such as that given by Landolt-Börnstein, are somewhat confusing because of the differences between the observations of different observers. Therefore, in arriving at the most probable value for any of these constants it is necessary to make a critical examination of the details of the measurements whenever possible. In Table 1 are

given the refractive indices of a number of the common gases. The values are all for a wave length of 589×10^{-6} mm (sodium or *D* line), since the data are most complete for this wave length and it represents fairly well the average wave length of the light used in the interferometer. The values given in this table have been found by taking the averages of the most reliable observations, and represent the author's judgment of the best values to use.

It will be noted that the refractivity values in this table are for gas at 0°C and under a pressure of 760 mm of mercury.

VI. REFRACTIVITY AT LOW PARTIAL PRESSURES

For small changes in pressure or temperature the density, and therefore the refractivity, can be calculated with sufficient accuracy by means of the gas laws, as indicated in equations (4), (5), and following. If, as is usually the case, a small percentage of a gas is being measured, its partial pressure will be small. If the deviation of the gas from Boyle's law is significant, the refractivity of the gas at this low partial pressure may differ from the value calculated from the ratio of the pressures. The correction necessitated by this fact will now be discussed.

The refractivity of a gas is the sum of the refractivities of its constituents. If the molecules in a mixture of gases could be sorted out and the refractivities of each kind totaled, the refractivity of the mixture could probably be ascertained with high precision. Because this is not possible, we have used in the discussion a larger unit of measurement, which is the number of molecules contained in a unit volume of the gas at a definite temperature and pressure. It is therefore necessary to know how the number of molecules in a unit volume varies with changes in temperature and pressure. This variation is given with close approximation for many gases by the simple gas laws. In order to calculate the number of molecules of each kind in a mixture of gases, we have further made use of what is known as Dalton's law.

Dalton's law, as commonly expressed, states that the pressure of a mixture of gases is equal to the sum of the pressures which each gas would exhibit if it occupied the total volume alone. In applying this law, we have assumed according to Boyle's and Avogadro's laws that the number of molecules in a unit volume is proportional to the pressure. If Dalton's law were strictly true, then the exact refractivity at any partial pressure could be calculated by using the observed expansion coefficients, or, what is the same thing, correcting the values calculated by Boyle's law for the

deviations from it. Dalton's law, just as Boyle's law, however, is strictly correct only for the limiting case of perfect gases. Consequently, a gas at a pressure of 1 mm does not necessarily have the same refractivity that it would if it had a partial pressure of 1 mm in a mixture of gases. The reason for this is that in a mixture of gases the attractive forces between different species of molecules come into play and modify the volume relations. The more nearly two gases resemble each other in their physical properties (critical temperature and pressure, density, etc.), the less effect deviations of the gases from Boyle's law have upon their partial pressures. As an illustration, it is obvious that a partial pressure of 1 per cent of carbon dioxide in carbon dioxide, if we can speak of such a thing, shows no deviation from Boyle's law, because it has exactly the same physical properties as the gas with which it is mixed, namely, carbon dioxide. However, a partial pressure of 1 per cent of carbon dioxide in air will show a certain deviation from Boyle's law.

The work of Berthelot,⁶ Fuchs,⁷ and others has shown that the mixing of two gases originally at the same temperature or pressure is accompanied by a small increase in pressure or volume. The change in volume is a minimum when the gases which mix are most nearly alike in their physical properties. It appears, therefore, that in most cases the deviations from Boyle's law at low pressures should be taken account of in calculating the refractivities of mixtures, at least until more data are available on this point. In the case of mixtures of two gases, such as oxygen and nitrogen, or carbon dioxide and nitrous oxide, which are very similar in their physical properties, the use of the observed refractivities will give the best results. In the case of dissimilar gases, the refractivities at low partial pressures should be corrected for the deviations from Boyle's law.

The discussion of this point has perhaps taken more space than its importance would warrant, but because these facts are usually overlooked in similar cases, it has been thought desirable to call attention to them.

The deviation of a gas from Boyle's law can be calculated with sufficient precision from Berthelot's equation of state for gases and vapors. Jones and Partington⁸ have calculated by means of Berthelot's equation what they call the "ideal refrac-

⁶ Berthelot, *J. de physique*, 8, 3 p. 521; 1899.

⁷ Fuchs, *Z. physik. Chem.*, 92, p. 641; 1918.

⁸ Jones and Partington, *Phil. Mag.*, 29, p. 28; 1915.

tivity" of the gas. The ideal refractivity is, in effect, the refractivity at 0° C and 760 mm calculated by means of Boyle's law from the refractivity at very low pressures. Consequently the refractivity of any gas at a low partial pressure can be more precisely calculated from this value by application of Boyle's law than from the observed value at 760 mm. The values for the ideal refractivity given in Table 1 should be used where the difference in refractivity caused by a small percentage of the gas is desired, subject to the conditions outlined in the preceding paragraphs.

VII. NOTES ON THE OPERATION OF THE INTERFEROMETER

In the use of the interferometer it will be noted that the readings are a function of the temperature and pressure. For the greatest convenience calibration curves should be drawn for different temperature and pressure intervals so that the correct reading can be obtained by interpolation. In the usual method of using the instrument and of calibrating with analyzed gas mixtures it is apparently customary to neglect the effect of temperature and pressure. It can be seen from the equations that if the readings are made at a temperature only 3° C higher or lower than the temperature at which the instrument was calibrated, they will be in error by 1 per cent. The errors from this source, if neglected, may easily be greater than any of the errors of calibration.

Another error in the use of interferometers which employ a glass compensator plate comes from the shift of the central white or achromatic fringe. This is due to differences in the relative dispersions of the gases and air and glass. L. H. Adams⁹ has analyzed this phenomenon for the Zeiss interferometer and developed equations by which the shift may be estimated. What takes place is that, as the concentration of a gas is changed, the edges of the central achromatic fringe gradually become colored and the original central fringe is no longer the most nearly achromatic fringe, provided the concentration change has been carried far enough. The result is in effect a shifting of the reference point.

The number of scale divisions through which the compensator must be turned to shift the achromatic fringe a distance of one band varies, of course, with every gas. The interval can be determined experimentally by increasing the concentration of

⁹ Adams, J., *Am. Chem. Soc.*, 37, p. 1181; 1915.

the gas in one chamber gradually and constantly, meanwhile keeping the original central fringe in line with the reference fringe. (See Chapter II on Principle of Method.) The concentration can be increased gradually by allowing the gas to enter the chamber through a small needle valve and slowly dilute the mixture. If at any scale reading the original central fringe is still the most nearly achromatic, no error can result from that cause, because it would still be aligned with the reference fringe to obtain the scale reading. The scale reading, when the achromatic fringe has shifted the width of one band, should be noted.

A portable interferometer was tested in this way with carbon dioxide, which has a considerably higher dispersion than hydrogen, nitrogen, oxygen, etc. There was no uncertainty as to which was the original central fringe until concentrations as high as 60 to 80 per cent of carbon dioxide were reached. This is well beyond the range of instruments with 100 cm gas tubes. Because of the low dispersion of most gases, no difficulty will usually be met with from this source when low concentrations, say 20 per cent or less, are being used. Furthermore, when there is any doubt as to whether or not a shift has occurred, it can be determined experimentally in the manner indicated.

VIII. ILLUSTRATIVE CASES

To illustrate the use of the equations and show how the sensitivity of the interferometer varies under different conditions of use and with different gases, a number of typical cases will be discussed. The ease and simplicity with which variations in ΔR and its equivalent, the scale reading, can be calculated for different conditions will be demonstrated. Although the instrument can in most cases be calibrated with analyzed mixtures, the method here described is usually as accurate, if not more so.

One of the most common uses of the interferometer is for the determination of carbon dioxide in mixtures of carbon dioxide and air. There are three typical cases which may be considered: First, a mixture of carbon dioxide and normal air is compared with normal air as a standard. Second, a mixture of carbon dioxide and air, in which there is a deficiency of oxygen, is compared with normal air; such mixtures may occur in mines, for example. Third, a mixture of carbon dioxide and air, in which there is a deficiency of oxygen, is compared with the residue remaining after the carbon dioxide has been removed by absorption.

FIRST CASE

The difference in refractivity between normal air and air containing the same proportion of nitrogen and oxygen, together with 1 per cent of carbon dioxide, at 20° C and 760 mm pressure can be calculated from equation (5).

$$\Delta r = \Delta R = \frac{273}{293} \cdot \frac{1}{100} (4467 - 2917) = 14.44$$

SECOND CASE

If 1 per cent of oxygen in the above mixture is replaced by 1 per cent of nitrogen, then R_2 , the refractivity of the air, is increased by 1 per cent of the difference between the refractivities of nitrogen and oxygen, and ΔR is apparently increased by the same amount, or

$$\frac{1}{100} \cdot \frac{273}{293} (2972 - 2706) = 2.48$$

The refractivity of the standard gas (air) remains constant. Accordingly the carbon dioxide, as indicated by the calibration in the first case, will be $\frac{2.48}{14.44}$ of the 1 per cent or 0.172 per cent too high for each change of 1 per cent of oxygen. For example, if the interferometer indicated 3.34 per cent carbon dioxide and the mixture contained 18.25 per cent oxygen there would be a deficiency of 2 per cent $[(100 - 3.34) \times 0.2094 - 18.25]$ in the air, and the corrected percentage of carbon dioxide would be $3.34 - (2 \times 0.172) = 3$ per cent. This calculation neglects the fact that the value for the percentage of air in the gas $(100 - 3.34)$ is only a first approximation; a closer approximation to the correct value is obtained by using the corrected figures for carbon dioxide, which gives $100 - 3.0 = 97$ per cent air. Using this value, the deficiency in oxygen is found to be 2.06 per cent, instead of 2 per cent, and the corrected percentage of carbon dioxide equals 2.99 per cent.

Burrell and Seibert¹⁰ determined this correction experimentally and made six observations (0.135, 0.103, 0.128, 0.155, 0.162, and 0.160), from which they concluded that each 1 per cent lowering of the oxygen content increased the apparent amount of carbon dioxide by 0.15 per cent. In calculating their values they subtracted the percentage of oxygen in the mixture from the percentage of oxygen in normal air (they use 20.93 per cent). It is

¹⁰ Bureau of Mines Bulletin No. 42, p. 73; 1913.

obvious, however, that the percentage of oxygen in the mixture varies with the amount of carbon dioxide present and the final value they calculate is, therefore, not a constant as assumed. Take their first observation: The mixture contained 0.50 per cent carbon dioxide and 20.19 per cent oxygen. The air present in the mixture is then 99.5 per cent and if it were normal air the percentage of oxygen in the mixture would be $99.5 \times 0.2093 = 20.82$, and the deficiency of oxygen, expressed as a percentage of the original mixture is $20.82 - 20.19 = 0.63$ per cent. The difference between the carbon dioxide indicated by the interferometer and by chemical analysis was 0.10 per cent. The error in the observed percentage of carbon dioxide for each per cent deficiency of oxygen is then $\frac{0.10}{0.63} = 0.159$ per cent, instead of 0.135, as calculated by their method. When calculated on this basis, the average of Burrell and Seibert's six experiments is 0.166 per cent, which is in fair agreement with the value 0.172 calculated in the preceding paragraph.

Burrell and Seibert¹¹ also concluded from six observations (0.174, 0.179, 0.138, 0.150, 0.167, and 0.179) that this figure was, for methane, 0.16 per cent for each per cent lowering of oxygen when normal air was used as standard. Their data recalculated on the correct basis give an average of 0.182 per cent which is in fair agreement with the theoretical value of 0.179.

THIRD CASE

The analysis of the third case, where the carbon dioxide is removed from the mixture before passing it into the second chamber to serve as the standard gas, is of especial interest because this method greatly reduces the errors due to other variations in the composition of the mixture and extends the use of the interferometer to other than strictly binary mixtures.

The effect of any variation in composition upon the difference in refractivity of the gases in the two chambers can be easily calculated. In the case at hand let R_1 be the refractivity of the constituent for which the calibration is sought and R_2 the refractivity of the standard gas which remains after removal of the first gas from the mixture. Also let R_3 be the refractivity of the gas, such as oxygen, nitrogen, etc., which dilutes the original mixture and also the standard gas. Then let a be the percentage of R_1 and b the percentage of R_3 which is present.

¹¹ Loc. cit.

The difference in refractivity between the two chambers when a per cent of the first gas is in one chamber is given by equation (5).

$$\Delta r = \frac{a}{100} \cdot (R_1 - R_2) \quad (5)$$

If b per cent of the gas having the refractivity R_3 is present, the difference in refractivity between the two chambers is as follows:

$$\Delta r_1 = \left[R_1 \frac{a}{100} + R_2 \frac{(100-a-b)}{100} + R_3 \frac{b}{100} \right] - \left[R_2 \frac{(100-a-b)}{100-a} + R_3 \frac{b}{100-a} \right] \quad (7)$$

In this equation the quantities in the two brackets are the refractivities of the gases in the two chambers. It should be noted that the change of b per cent of the third gas in the mixture corresponds to a change of $\frac{b}{100-a}$ in the residue after a per cent of the first gas has been removed. Equation (7) simplifies to

$$\Delta r_1 = \frac{R_1 a}{100} - \frac{a}{100^2 - 100a} \left[R_2 (100-a-b) + R_3 b \right] \quad (8)$$

Subtracting equation (8) from (5) to determine the difference in Δr , with and without the third gas, we have

$$\Delta r - \Delta r_1 = \frac{ab}{100^2 - 100a} (R_3 - R_2) \quad (9)$$

Equation (9) can be written by inspection when the relations involved are understood; however, it is developed in the above manner in order to make each step clear.

The effect on the indicated percentage of carbon dioxide in air, when the composition of the air varies, can now be calculated. If a , the percentage of carbon dioxide, and b , the change in percentage of oxygen from normal (20.94 per cent), are both 1, then at 20° C

$$\Delta r - \Delta r_1 = \frac{273}{293} \cdot (2706 - 2972) \cdot \frac{1}{9900} = -0.025.$$

ΔR for 1 per cent of carbon dioxide in air under the conditions of the first or normal case is 14.44; the observed reading under the conditions of the third case is accordingly $\frac{-0.025}{14.44}$ of the

1 per cent, or 0.0017 per cent, too low. When normal air was used as the standard gas, each decrease of 1 per cent of oxygen raised the apparent amount of carbon dioxide by 0.172 per cent.

In the cases just cited there was a deficiency of oxygen. The case in which there is an excess of oxygen in the air is also met with in practice and is treated in a similar manner. This condition occurs in the analysis of gas from a balloon or airship having an envelope of rubberized fabric. Because of the higher permeability of rubber to oxygen than to nitrogen the air penetrating rubber may contain as high as 41 to 42 per cent oxygen.¹² This fact should be taken account of in all analyses of gases from balloon envelopes.

CHOICE OF STANDARD GAS

It may be remarked in passing that the character of the standard gas has no relation to the sensitivity of the interferometer. It merely provides a standard constant refractivity from which differences may be measured. A change of 1 per cent of carbon dioxide in air produces the same difference in scale reading (providing the scale is linear) whether air or carbon dioxide or any other gas is the standard. It makes a great practical difference, however, in convenience and accuracy as to what gas is used as the standard. Take the case of carbon dioxide in air. If 1 per cent of carbon dioxide in air is compared with air as a comparison gas, then Δr , the difference in refractivity between the two

chambers is equal to $\frac{1}{100} \times 1444$ at 20° C and 760 mm pressure.

If carbon dioxide is used as a comparison gas the difference in refractivity between the two chambers is equal to $\frac{99}{100} \times 1444$. In

the first case, a change of 1 per cent in temperature or pressure makes a difference in Δr (see equation 5) corresponding to 0.01

per cent carbon dioxide $\left(\frac{0.14}{14.44}\right)$. In the second case such a

change in temperature or pressure makes a difference in Δr corresponding to 0.99 per cent carbon dioxide $\left(\frac{0.01 \times 0.99 \times 14.44}{14.44}\right)$

which is almost as much as the quantity being determined (1.00 per cent).

¹² See article by Edwards and Ledig on "The Significance of Oxygen in Balloon Gas," *Aviation*, 6, p. 325; 1919.

It is thus apparent that the greatest freedom from error due to changes in temperature and pressure is secured when the difference in refractivity between the mixture and the standard gas is a minimum. This condition is usually met when the major constituent of the mixture is used as the standard gas; the zero reading of the interferometer then corresponds to a zero difference in optical path between the two tubes.

ANALYSIS OF FLUE GAS

The interferometer has been suggested and used for the analysis of flue gas. The situation in this case is rather complex because of the number of gases which may be present in the mixture. Usually the percentage of carbon dioxide in a flue gas is determined because it is an index of the proper firing conditions. The flue gas can be considered to be a mixture of carbon dioxide and nitrogen with varying amounts of oxygen, carbon monoxide, hydrogen, methane, and water vapor, depending upon the fuel used, the completeness of combustion, etc. It is interesting to analyze the conditions and show what the error would be with any combination of gases.

The best method of operation, of course, is to absorb the carbon dioxide after passing the gas through one chamber and to use the residue as a standard of comparison. Take the case of a furnace gas of the composition shown in Table 2. In this example carbon dioxide is the gas sought, and the residue, after the absorption of the carbon dioxide, is assumed to be nitrogen (considering the argon present as nitrogen), with the other gases as diluents. In Table 2 are tabulated the corrections to ΔR calculated according to equation (9).

TABLE 2.—Corrections to Indicated Percentage of Carbon Dioxide for a Certain Furnace Gas

Constituent	Per cent present	$\Delta R \times 10^{-7}$	$\left(\frac{ab}{100^2 - 100a}\right) \Delta R \times 10^{-7}$
CO ₂	13.5	CO ₂ -N ₂ =+1498
O ₂	2.0	O ₂ -N ₂ =- 266	-0.83
CO.....	4.6	CO -N ₂ =+ 375	+2.69
CH ₄	0.2	CH ₄ -N ₂ =+1436	+0.45
H ₂	1.4	H ₂ -N ₂ = -1585	-3.46
N ₂	78.3
Net correction equals.....		=1.15

The corrections in the last column are calculated in the manner indicated. The value for the 2 per cent of oxygen for example is

$$\frac{2 \times 13.5}{10\,000 - 1350} \times 266 = -0.83. \quad \text{The error in the reading for } 13.5$$

$$\text{per cent carbon dioxide is } - \frac{1.15}{14.98 \times 13.5} = -0.0057 \text{ or the per-}$$

centage of carbon dioxide indicated by the interferometer will be $13.5 - (0.0057 \times 13.5) = 13.42$ per cent CO_2 . The amount of this correction is entirely negligible in any flue-gas analysis. Mohr¹³ has analyzed a number of flue gases and found that the percentage of carbon dioxide as determined with the interferometer agreed within the limits of the instrument (0.1 per cent CO_2) with the values found by the usual method of gas analysis by absorption. The errors of the interferometer were of the order indicated by the theory discussed above.

The carbon monoxide and methane in the furnace gas could also be determined by first removing all the carbon dioxide and then oxidizing the carbon monoxide and methane with hot copper oxide. The carbon dioxide formed in the gas mixture could then be determined in the manner just outlined, and this percentage would be equal to the sum of the percentages of carbon monoxide and methane originally present.

Kreisinger, Augustine, and Ovitz¹⁴ have found that the combustible gases in furnace gas, other than carbon monoxide, consist mainly of hydrogen; methane and other hydrocarbons occur only in traces. Furthermore, the carbon monoxide constitutes about 80 per cent of the total combustible gases. These observations are of interest in connection with the subject of flue-gas analysis.

DETERMINATION OF HELIUM IN MIXTURES

The interferometer was found useful in the analysis of a sample of helium produced by the fractional liquefaction of natural gas; the details of the analysis are of interest because they illustrate the use of the methods already discussed. From the method of manufacture, the gas was known to consist of helium and nitrogen with smaller amounts of methane. Tests showed the absence of oxygen in the mixture. Because of the presence of three constituents, the readings of the interferometer alone are not determinate.

¹³ Mohr, *Zs. angew. Chem.*, 25, p. 1313; 1912.

¹⁴ Bureau of Mines Bulletin 135, p. 107; 1917.

Accordingly the methane (other hydrocarbons assumed to be absent) was determined in a separate sample by combustion with oxygen over a heated platinum wire; the amount found was 0.2 per cent. The interferometer gave a reading of 1577 scale divisions when the mixture was compared with air. The calibration of the interferometer showed this to be equivalent to a Δr of 2421×10^{-7} at 0°C and 760 mm pressure. The refractivity of the mixture is then equal to $2917 - 2421 = 496 \times 10^{-7}$. If X equals the percentage of helium present then the refractivity of the mixture is also given by the following relation (see equation (3)).

$$X(342) + (1.00 - X - 0.002)(2972) + 0.002(4408) = 496$$

$$X = 0.943$$

The complete analysis is then as follows:

	Per cent
Helium.....	94.3
Nitrogen.....	5.2
Methane.....	0.2
	<hr/> 100.0

The analysis made in this way was checked by using the density of the mixture and its constituents in place of the refractivity. This latter method indicated the presence of 94.6 per cent helium in the mixture. The difference is only 3 parts in 1000, which is quite a satisfactory agreement. It is much simpler and quicker, however, to determine the refractivity with the interferometer than to determine the density with the necessary accuracy.

Another sample of helium analyzed in the same manner with the interferometer showed the following composition:

	Per cent
Helium.....	53.6
Nitrogen.....	34.5
Methane.....	11.9
	<hr/> 100.0

The percentages of helium and nitrogen were also calculated from the density of the mixture and found to be 53.4 and 34.7, which is also a very satisfactory agreement considering the nature of the problem.

IX. SENSITIVITY OF INTERFEROMETER

The sensitivity of the interferometer depends on the length of the gas chambers and certain other constants of the instrument. The Zeiss portable interferometer with 10 cm tubes indicates

about 0.1 per cent carbon dioxide in air for each small scale division. The laboratory type with 100 cm chambers indicates about 0.01 per cent carbon dioxide. The relative sensitivity of the instrument for different gases is shown in Table 3. It is assumed that each scale division indicates 0.01 per cent carbon dioxide. The percentage of other gases in certain mixtures, which is indicated by each scale division, is shown in the last column.

TABLE 3.—Relative Sensitivity of Interferometer for Different Gases

Constituent to be determined	Composition of mixture	$\Delta R \times 10^{-7}$ for 1 per cent of gas at 0° C—760 mm	1 scale division indicates per cent
Carbon dioxide.....	CO ₂ —Air	15.50	0.0100
Methane.....	CH ₄ —Air	14.91	.0104
Hydrogen.....	H ₂ —Air	15.29	.0101
Oxygen.....	H ₂ —O ₂	13.18	.0118
Do.....	O ₂ —N ₂	2.66	.0583
Nitrogen.....	O ₂ —N ₂	2.66	.0583
Helium.....	He—N ₂	26.30	.0059
Ammonia.....	NH ₃ —Air	8.61	.0180
Acetylene.....	C ₂ H ₂ —Air	30.54	.0051

Many other interesting cases could be discussed; the present examples, however, are typical of those met with in practice and illustrate the use of the equations and the method of determining the suitability of the interferometer for any specific purpose.

X. SUMMARY

The principle of the gas interferometer and its method of use in gas analysis is discussed in connection with the calibration of the instrument. The effect produced upon the observations by variations in gas composition and experimental conditions is analyzed and equations developed by which the magnitude of such changes can be estimated. Typical cases in which the interferometer may be employed, such as for the analysis of mixtures containing helium, analysis of flue gas, etc., are given together with points on sources of error, details of operation, and the relative sensitivity of the interferometer for different gases.

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